

# Wheat Straw as a Paper Fiber Source



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The chemical and morphological variations within the straw plant and between commercial cultivars were examined. Six commercial cultivars (Madsen, Eltan, Stephens, Lewjain, Cashup, and Rod) were hand harvested from an experimental, irrigated plot in Moses Lake, Washington. Four within-field replicates of Madsen were collected and analyzed.

As expected, the average fiber length of the Moses Lake (irrigated) straw had weighted average fiber lengths around 0.1 mm longer than straw grown in dryland conditions. With the Moses Lake samples, the variation within the field was greater than the cultivar variation; therefore, no variation could be distinguished between cultivars. However, great differences in fiber length distribution were seen within the plant. The leaf and node sections contained more fines and less long fibers than the internodal sections. Pulping of only the internodal sections should reduce the fines content and improve drainage of the pulp.

The leaves, nodes, and internodes (stems) of each plant were hand sorted and their chemical compositions were determined. The leaf fraction contained more silica than the internodes and nodes, thus showing a benefit of leaf removal before pulping. Variation was seen between cultivars with Eltan leaves containing less silica than the other leaves. The internodal and nodal sections of Cashup straw contain more silica than the other cultivars. These variations may suggest an opportunity to upgrade the raw material through selective harvesting and possible avenues for genetically altering the wheat.

Madsen wheat straw variety was pulped by vapor phase and by liquid phase conditions after presteaming of dry, chopped straw. The former uses short impregnation and cooking times with direct steam heating. At optimum conditions plant stem nodes comprise the major part of 5% rejects stream. This offers a chance to purge the nodes and associated fines and silica from the system. Liquid phase pulping used longer times and higher water and chemical charges. The rejects levels were less than 1% as a result of improved impregnation. Total yields were about 1% less than vapor phase pulps at the same kappa.

Bleaching conditions for the vapor phase pulps resulted in  $80 \pm 2$  brightness unites. The soda/AQ and soda oxygen pulps bleached with about the same effort and similar properties. Since low reject, liquid phase pulps seem to be of most interest, they were bleached to 86+ brightness with an overall bleached yield of about 40 percent. Unbleached and bleached viscosities were 32 and 20 cP, respectively, and physical properties of pure straw pulps were similar to literature values.

Wheat straw pulp will likely be used in blends with wood pulps in proportions consistent with paper and board cost and performance specifications. For example, high-brightness communication papers are produced by Domtar, Inc., from recycled old corrugated containers (OCC) which have been pulped and bleached. The pulp, referred to as Crystal pulp, can be blended with bleached wheat straw pulp to produce similar products. Blends of straw and Crystal pulp increase in density with higher proportions of wheat straw. The fiber size distribution of these two pulps are similar, but the latter contains somewhat larger amounts of the longer fraction. As a result, furnishes with larger proportions of Crystal pulp have substantially higher tear. Tensile values change only a small amount with furnish composition.

Straw black liquor viscosities are substantially different than in wood-based kraft liquors. In the range of 20 to 40% solids and up to 70°C, straw liquor capillary viscosities exceed wood based liquors by a factor of 2 to 3. Very little sludge deposits were formed in that solids content range.

The straw black liquor heating values were about 6300 Btu/lb. and fall within the range expected for kraft liquors. Most of the metals tested are within expected ranges with the exception of potassium. That element is present in straw in high concentrations which accounts for the high black liquor levels. Black liquor silica concentrations (170 ppm) fall well below many literature reports, but the steady state level in mill recovery circuit will probably be considerably higher.

Nonwood fibers have a long history as a raw material for papermaking. The use of this raw material declined in Europe and North America during the first half of this century as the amount of inexpensive and readily available wood fiber increased. Currently China produces about one-half of the world's nonwood pulp while Europe and North America are relatively small contributors (FAO, 1995). These two regions consume about 60% of the world pulp and paper production. Only four modern straw/grass fiber production sites exist in Europe and none in the United States. In some situations however, nonwood plants may prove a viable fiber source in these industrialized regions.

Environmental and population growth pressures are contributing to long-range changes in forest land management practices which reduce harvest of wood for wood products and for pulp and paper manufacture (Bruenner, 1994). At the same time cereal grain crop production in the United States generates tremendous quantities of straw. For example, three million acres of wheat are grown in Washington state each year producing about three tons of straw per acre. While 0.5 tons of straw per acre are required to be maintained on the soil surface for erosion control of steeply sloped ground (Veseth, 1987), the excess straw often presents problems for subsequent field operations such as no-till seeding. Therefore, straw may represent a significant fiber substitution opportunity. For example, pulp from cereal grain straw may partially substitute for wood fiber in a range of paper and paperboard products.

Yet the utilization of this fiber source in North America has several potential limitations. The foremost include small fiber dimensions, limiting the strength of paper products (Misra, 1987) and paper machine operating speeds. The high inorganic content of straw creates potential problems in conventional chemical recovery systems (Misra, 1987). Blends of straw and wood pulps can provide useful paper properties; however, better understanding of straw properties will be the basis for future developments using significant amounts of this raw material in North American mills.

This work demonstrates that Washington state wheat straw could be successfully pulped by soda/AQ chemistry and bleached by the DE<sub>0</sub>D sequence to fully bleached levels at about 40% yield based on oven dry straw. Paper physical properties in Crystal pulp blends fit the needs for producing fine and communication papers.

This project was organized in the three phases shown below.

Phase 1	Chemical and Morphological Variation in Pacific Northwest (PNW) Wheat Straw
Phase 2	Pulping (NaOH/AQ and NaOH/O <sub>2</sub> ) and Bleaching (DE <sub>0</sub> D) of Whole Madsen Straw
Phase 3	Black Liquor Characterization, Pulp Refining, Blending with Bleached OCC Pulp, and Paper Testing

The discussion of results follows that pattern.

## 2.0 Wheat Straw Characterization

### 2.1 Background

Properties of papermaking fibers from wood or from annual crops can be influenced by both growing conditions and genetic manipulation. For example, many studies show that wood morphology and chemical composition vary with location, genetics, and growth conditions. The chemical composition of both eucalyptus [Beadle *et al.*, 1996] and rice straw [Kuo and Shen, 1992] has also been found to vary with growing location. Similar trends occur when comparing wheat straw chemistry and morphology from different sources. For example, reports shown in Table 1 show that carbohydrate contents vary about  $\pm 5\%$  (absolute), lignin  $\pm 2\%$ , ash  $\pm 3\%$ , and silica and extractables in similar amounts. The origin of these variations may be due to genetics or growth conditions but is not apparent in the reported work.

Table 1. The Chemical Composition of Wheat Straw

	Ali <i>et al.</i> [1991] Pakistan	Aronovsky <i>et al.</i> [1948] Illinois	Mohan <i>et al.</i> [1988] India	Utne & Hegbom [1992] Norway	Misra [1987] American	Misra [1987] Denmark
holocellulose	58.5					72.9
$\alpha$ -cellulose	33.7	34.8		29-35	39.9	41.6
hemicelluloses	25.0	27.6	28.9	26-32	28.2	31.3
lignin	16-17	20.1	23.0	16-20	16.7	20.5
ash	7.5-8.5	8.1	9.99	4-9	6.6	3.7
silica & silicates	4.5-5.5		6.3	3-7		2.0
EtOH-Benzene extr.	5.8	4.5	4.7		3.7	2.9

Like chemical content, straw cell dimensions are believed to vary with soil and growth conditions [Utne and Hegbom, 1992]. Table 2 lists some of the reported wheat cell dimensions. Clearly, wide ranges of properties occur in the published literature. Some may be real, but some may depend on measurement technique. For example the difference in fiber length between Cheng and coworkers [1994] and Hua and Xi [1988] is extreme. A possible explanation for the difference in values could be that Cheng counted all of the cells while the other authors only included the fibers in their measurements.

## 2.0 Wheat Straw Characterization

**Table 2. Morphology of Wheat Straw**

	Avg Length (mm)	Avg. Diam. ( $\mu$ m)	NAFL (mm)	WAFL (mm)	MWAFL (mm)
Atchison & McGovern [1987]	1.5	15			
Cheng <i>et al.</i> [1994]			0.26	0.63	1.09
Hua & Xi [1988]		12.9	1.32	1.49	
Mohan, <i>et al.</i> [1988] (incl. min. - max.)	1.5 0.7 - 3.1	13.3 6.8 - 24.0			
Utne and Hegbom [1992]	1.3	13			

NAFL -- Numerical Average Fiber Length; WAFL -- Weighted Average Fiber Length;  
MWAFL -- Mass Weighted Average Fiber Length

Since comparing reported values is difficult, several studies have specifically looked at the effects of growing conditions on fiber morphology. Using common sisal and a hybrid, Gerischer and Bester [1993] found different chemical compositions and different refining behavior which he speculated to be due to differences in coarseness. Ravn [1993] examined wheat straw and found differences in pulping and papermaking characteristics between varieties. However, such studies have not been done for the different growing conditions and commercial cultivars in the PNW. Since straw from irrigated farms has higher WAFL than dryland straw [Jacobs *et al.*, 1996], the present study focused on only one irrigated location (Moses Lake, Washington) and six of the more popular commercial cultivars (Table 3).

**Table 3. Commercial Cultivars Examined**

Cultivar	Acres (%) <sup>*</sup>
Madsen	22.1
Eltan	14.7
Stephens	10.5
Lewjain	6.5
Cashup	2.2
Rod	1.3

1995 Washington State Use (Hasslen, 1995)

Many of the literature reports are limited to the description of whole plant morphology and chemical differences. In addition, leaf, node and stem fractions may have different composition. The plant parts contribute significantly different mass as shown in Table 4.

## 2.0 Wheat Straw Characterization

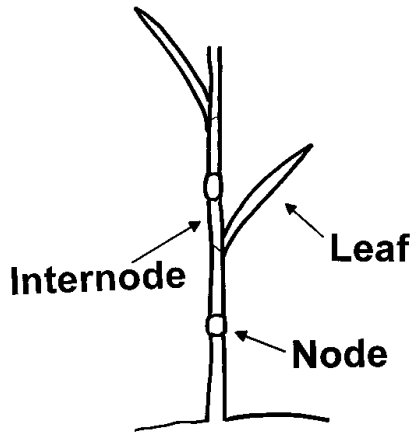


Figure 1. Sketch of Wheat

Table 4. Physical Content of Wheat

	Mass Percent*
Internodes	68.5
Leaves--Sheaths	20.3
Leaves--Blades	5.5
Nodes and Fines	4.2
Grain and Debris	1.5

\*Ernst *et al.*, 1960

Since the distinct sections of the plant have different functions, each section may also have different cells and chemical compositions. Table 5 summarizes the results of Billa and Monties [1995] and Zhang and coworkers [1990]. When examining European wheat straw, Billa and Monties found the acid insoluble lignin (Klason lignin) content of the internodes to be higher than the leaves and nodes. Klason lignin is only part of the total lignin content with soluble lignin being the other part. Billa and Monties did not report the soluble lignin content of the different fractions.

Table 5. Chemical Composition within Wheat Straw

	Internodes	Nodes	Leaves
Klason Lignin (%) <sup>1</sup>	18.9±0.1	14.8±0.2	13.5±0.2
Total Lignin (%) <sup>2</sup>		23.22	17.48
Holocellulose (%) <sup>2</sup>	71.24		56.95
Ash (%) <sup>2</sup>	5.93		12.06
Fiber Length (mm) <sup>2</sup>	1.73	0.82	

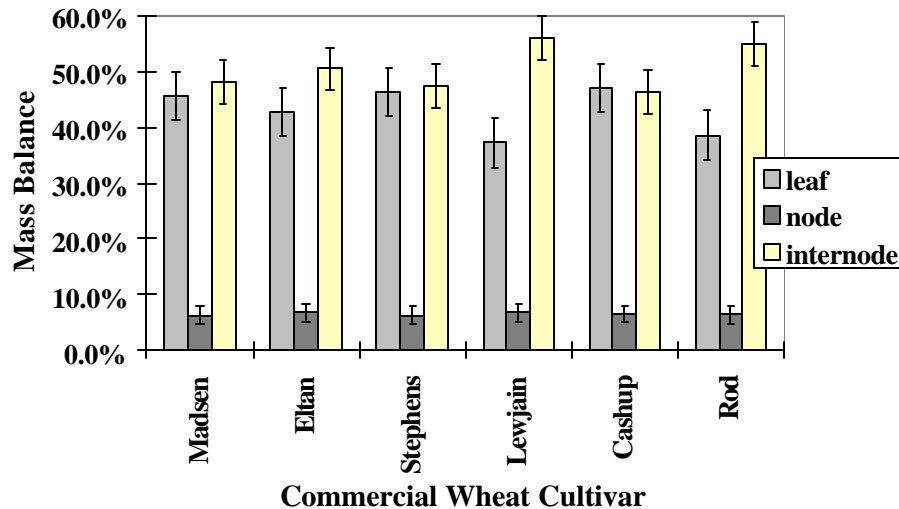
1. Billa and Monties, 1995

2. Zhang, *et al.*, 1990

With Chinese wheat straw, Zhang and coworkers found the stem section to have higher fiber lengths than the nodes, higher holocellulose, and less ash than the leaves. These trends suggest improved raw material qualities for the internodes, thus a potential for upgrading the raw material by fractionating out wheat straw components with less desirable properties. Phase 1 of this study will examine the potential benefit of within plant and between cultivar fractionation on PNW wheat straw.

### 2.2 Mass Balances

As mentioned above, Ernst and coworkers [1960] found their baled wheat straw to contain predominately internodes. However, this was not the case with our hand-harvested samples. As shown in Figure 3, the mass of leaves was comparable to that of the internodes.



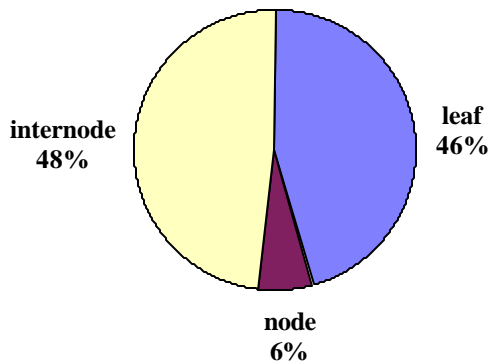
Error Bars are 95% Confidence Intervals Based on In-Field Variation of Madsen, Moses

**Figure 3. Mass Balance of Straw Fractions**

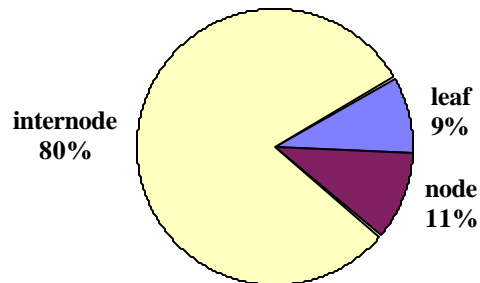
While the node content remained constant through the different cultivars (~6%), some variation was seen in the leaf and internode contents. One set of extremes is the Lewjain and Rod cultivars which clearly had more internodal material than leaves. If these trends carried through after mechanical harvesting, Lewjain and Rod may be better suited to whole straw pulping.

Mechanical harvesting of the grain breaks off some of the leaves. Using 9% leaf content as a common reference for straw after mechanical harvesting, one can estimate the content of node and internode after mechanical harvesting (Figures 4 and 5). Note that the estimated leaf content (9%) is lower than the 26% reported by Ernst and coworkers (1960). This discrepancy should be further examined. Hand sorting after baling would need to be done to confirm the 9% estimate. Even then, such a test may not hold for all commercial cultivars since some have more brittle leaves than others.

## 2.0 Wheat Straw Characterization



**Figure 4. Hand-Harvested Madsen**

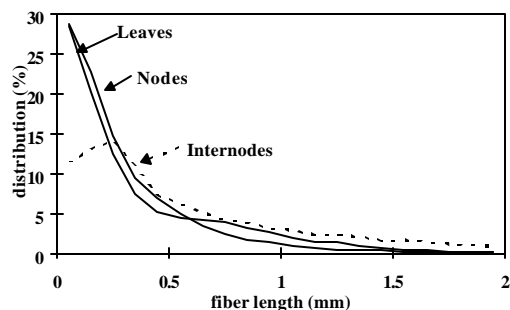


**Figure 5. Baled Madsen (Estimated)**

While the straw fractions did not vary within the field, the different commercial cultivars examined did have different quantities of leaves. All of the cultivars from this hand-harvested study had high quantities of leaves. This leaf content would be reduced when the straw is harvested mechanically and baled.

### 2.3 Fiber Length Distribution -- Within the Plant

Since the different sections of the plant have different functions, one may anticipate that the sections contain different cells and different cell distributions. Figure 6 and Table 6 describe the fiber length distribution within the Madsen cultivar.



**Figure 6. Fiber Length Distribution within the Plant (Madsen)**

**Table 6. Fiber Length within Plant (Madsen)**

	Mass (%)	NAFL (mm)	WAF L (mm)	Fines (%)
Whole		0.48	1.04	51.3
-Internodes	49	0.61	1.20	24.3
-Leaves	45	0.35	0.79	49.0
-Nodes	6	0.28	0.65	51.4

The internodal section of the plant seems to have a different fiber length distribution than the other two fractions with the internodal section containing less fines and more long fibers. The numerical average fiber lengths (NAFL) and weighted average fiber lengths (WAF L) reported for the whole straw in Table 6 is for the hand-harvested sample. If the proportions of nodes, internodes and leaves in mechanically-harvested straw were similar to those estimated in Figure 5, the NAFL may increase from 0.48 mm to 0.55 mm.

## 2.0 Wheat Straw Characterization

Further fractionation of leaf and nodes from the internodal section may improve the fiber length distribution by reducing fines. Since these fines are speculated to reduce papermachine speed and washing efficiency, such steps may be beneficial in some production lines.

### 2.4 Fiber Length -- Commercial Cultivars

While the fiber length distribution of wheat straw can be upgraded by removing the nodes and leaves, a variation between cultivars was not detected. Table 7 lists the fiber length and coarseness of the acid-chlorite, internodal pulps.

**Table 7. Fiber Length and Coarseness of Acid-Chlorite, Internodal Pulps**

	NAFL (mm)	WAFL (mm)	MWAFL (mm)	Coarseness (mg/100m)	Fines (%) (< 0.2 mm)
Madsen-1	0.49	0.94	1.29	2.77	32.86
Madsen-2	0.55	1.12	1.64	3.40	26.07
Madsen-3	0.51	1.00	1.43	3.23	29.83
Madsen-4	0.48	0.91	1.23	3.03	32.53
Eltan	0.45	0.90	1.31	2.93	34.08
Stephens	0.47	0.96	1.39	3.30	32.12
Lewjain	0.46	0.92	1.36	2.73	32.88
Cashup	0.47	0.90	1.27	2.80	32.54
Rod	0.51	1.08	1.59	3.47	28.76

The in-field variation in fiber length seemed drastic with Madsen WAFL varying from 0.91 - 1.12 mm. Such extreme variation in WAFL may represent (1) a strong dependence of fiber length on local soil conditions which vary within a field, (2) variation in fiber length distribution within the plant and a need for more uniform sampling of the different internodal sections within the plant, or (3) lack of reproducibility in the delignification procedure used to make the pulp samples. With the high in-field variation of the average fiber lengths, differences between commercial cultivars could not be found.

Since the six cultivars used in this study were all collected from an irrigated location in Washington state, it is useful to compare them to samples collected from different areas and growing conditions. While such data are limited, Cheng and coworkers [1994] also reported average lengths for all of the cells in his pulp. His results, listed in Table 2, stated a WAFL of 0.63 for wheat straw. When comparing this fiber length to the range of WAFL found with the 1996 Moses Lake straw, 0.90-1.21 mm, a drastic difference can be seen with the 1996 Moses Lake internodal straw giving much higher WAFL.

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Jacobs and coworkers [1996] reported a variation in internodal WAFL with stem height in developmental wheat cultivars. These developmental cultivars were grown in dryland conditions with stem heights ranging from 33-121 cm. The stem heights of the 1996 Moses Lake (irrigated) commercial cultivars ranged from 89-102 cm. This commercial cultivar range is superimposed on the results of Jacobs and coworkers in Figure 7.

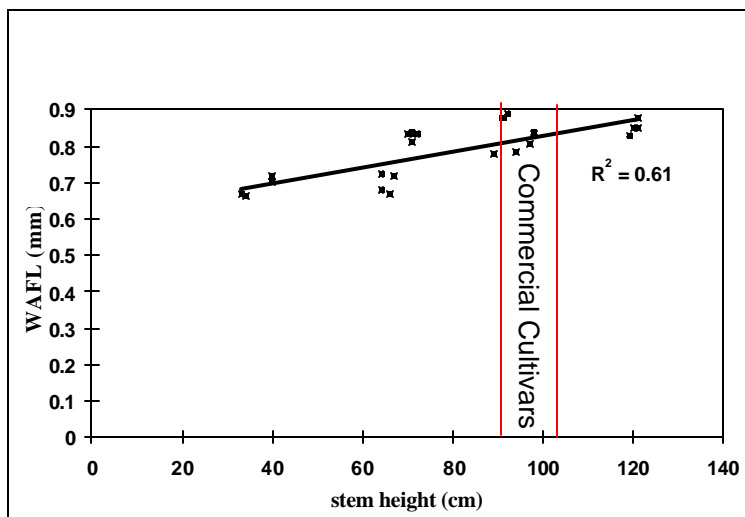


Figure 7. Developmental Wheat Cultivars (Dryland)

The data points in Figure 7 are those of the dryland developmental wheat cultivars. The commercial irrigated WAFL, ranging from 0.90 - 1.21 mm, would be around 0.1 mm greater than the developmental WAFL and off of the y-axis of Figure 7. Jacobs and coworkers [1996] also found irrigated wheat straw pulps to have around 0.1 mm higher WAFL than those grown in dryland conditions.

Changes in WAFL of 0.1 mm can influence the strength properties of a pulp. While a difference in average fiber length was not seen between the commercial cultivars, the irrigated, commercial cultivars examined did have higher WAFL than reported for dryland locations.

### 2.5 Cell Diameter

Generally larger diameter fibers result in better zero span tensile and can contribute to better fiber bonding and paper stiffness, tear, and tensile. Pulp from most annual crops have mean fiber diameters much less than softwood and slightly less than hardwoods.

Wheat straw contains a broad range of morphological structures with a wide range in dimensions. For example, typical diameters for wheat cells are: tracheids, ~5-24 $\mu$ m;

## 2.0 Wheat Straw Characterization

parenchyma cell, ~58-142  $\mu\text{m}$ ; and vessels, ~42-79  $\mu\text{m}$ . Clearly, diameter averages will depend on the structures selected for measurement. For example, if all of the cells are measured, different diameter distributions and averages are obtained than when only the tracheids are measured. Figure 8 compares the cell diameter distribution when counting all cells and when just counting the tracheids. When only tracheids' diameters were measured for the Eltan cultivar, the average fiber diameter was 18.6  $\mu\text{m}$  (compared to 45.8  $\mu\text{m}$  when counting all of the cells).

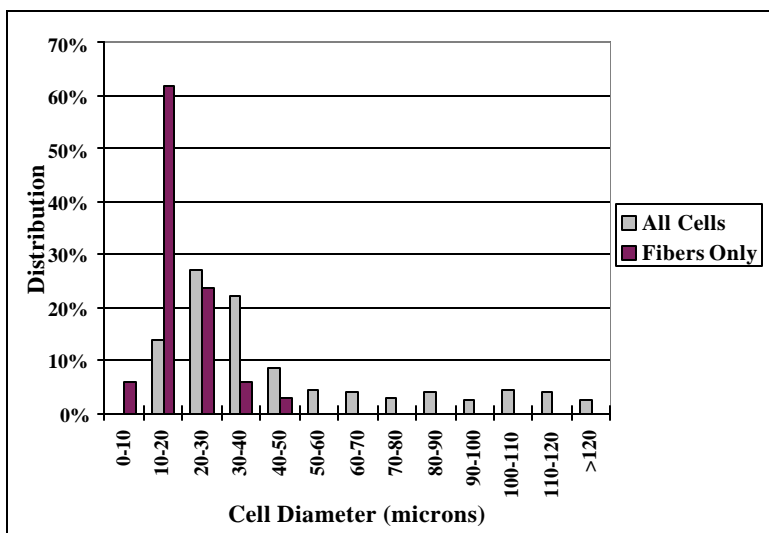
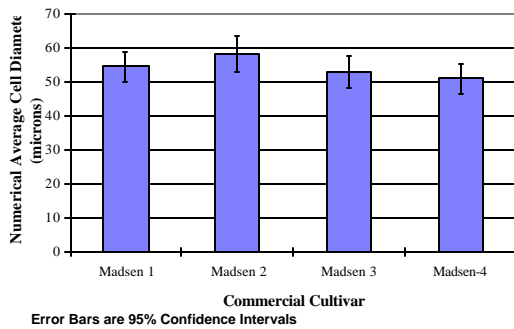


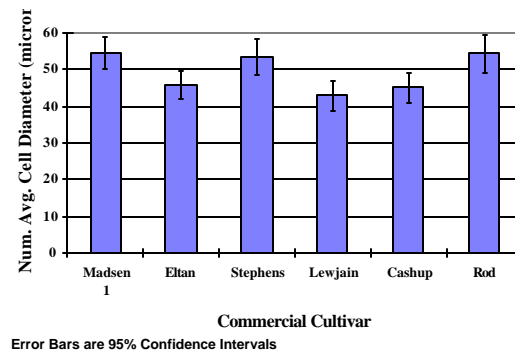
Figure 8. Diameter Distributions

When comparing the cultivars and in-field variation, all cells were included in the averages. The cell diameter distribution within the field for Madsen is illustrated in Figure 9. Since the 95% confidence intervals overlap, no difference was seen between these pulp samples. When comparing the different cultivars, Figure 10, the Madsen, Stephens, and Rod cultivars had higher average cell diameters than Eltan, Lewjain, and Cashup. This difference in average cell diameters may be due to wider cells or to a larger quantity of parenchyma and vessels in these cultivars.

## 2.0 Wheat Straw Characterization



**Figure 9. In-Field Variation of Cell Diameter**



**Figure 10. Cell Diameter Variation**

As alluded to above, all of these cell diameter averages (40-55  $\mu\text{m}$ ) are much higher than those reported in the literature for fiber diameters (averages from 12.9-15  $\mu\text{m}$ ). This comparison demonstrates: 1) the wide range in cell diameters, 2) the proportionately more low L/D material in straw than in softwood and hardwood, and 3) the potential need for tracheid diameters to be compared between the cultivars.

Straw is an interesting papermaking raw material. Straw pulp has a broader fiber length distribution than hardwood and a broader distribution in L/D (Runkel ratio) than hardwoods and softwoods. The examination of potential uses in paper/paperboard furnishes on the basis of physical/optical properties will be a subject of Phase 3.

### 2.6 Chemical Composition

The last portion of Phase 1 was a comparison of the chemical composition within the straw and between commercial cultivars. The chemical composition of the different straw fractions may provide some insight into the ease of pulping different fractions and the source of troublesome components like silica. Identification of any variation between cultivars may aid in identifying hybrids which are easier to pulp or contain less non-process elements. The chemical composition results are summarized in Table 8.

The Total (%) column of Table 8 should total 100, but in several cases does not. Lower results may be due to a variety of factors. (1) A comprehensive ash balance was not done to determine which components contained ash (like hemicellulose). Reporting ash-free carbohydrate and lignin contents may aid in solving this discrepancy. (2) The extractives may not all be counted. (3) Some carbohydrates may have been lost from the

## 2.0 Wheat Straw Characterization

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holocellulose if conditions for acid chlorite treatment were too severe. Further investigation would need to be conducted to resolve this discrepancy.

The extractives content is quite low compared to the ethanol-benzene extractives contents reported in Table 1. Two factors may have caused our results to be low. Table 8 lists acetone extractives. More extractives are soluble in ethanol-benzene mixtures than acetone. Another possibility is that the eight cycles on the Soxhlet may not have been sufficient to remove all of the acetone extractives from the straw.

The ash content of the leaves and nodes appeared to be similar while the ash content of the internodes was lower than the leaves and often the nodes (Figure 11). When comparing acid insoluble ash (silica and silicates) (Figure 12), the nodes and internodes were in the same range. However, the leaves contained much more silica and silicates. The similar silica contents in the nodes and internodes match the findings of Roy and coworkers [1993] who found silica in rice straw concentrated all along the stem rather than being confined to the nodes.

## 2.0 Wheat Straw Characterization

**Table 8. Chemical Composition of PNW Wheat Straw**

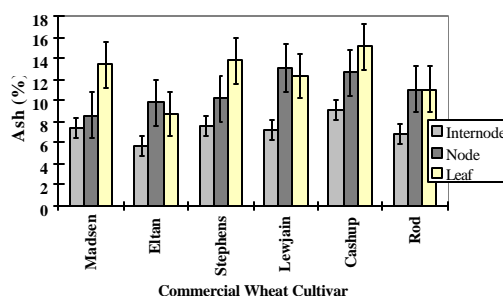
Internodes						
	<u>Cellulose (%)<sup>1</sup></u>	<u>Hemicellulose (%)<sup>1</sup></u>	<u>Lignin (%)<sup>1</sup></u>	<u>Extractives (%)</u>	<u>Ash (%)</u>	<u>Total (%)<sup>2</sup></u>
Madsen	36.7±1.2 <sup>4</sup>	34.7±2.5	18.0±2.0	1.1±0.1	7.4±0.9	97.8
Eltan	35.7	31.2	19.5	1.1	5.7	93.2
Stephens	35.7	35.3	19.0	1.0	7.6	98.6
Lewjain	35.2	32.3	18.9	1.0	7.2	94.6
Cashup <sup>3</sup>	48.3	20.4	19.7	1.1	9.1	98.5
Rod	35.3	35.2	20.3	0.9	6.8	98.5
Nodes						
	<u>Cellulose (%)</u>	<u>Hemicellulose (%)</u>	<u>Lignin (%)</u>	<u>Extractives (%)</u>	<u>Ash (%)</u>	<u>Total (%)</u>
Madsen	37.8	24.1	15.7±1.5	0.8±0.1	8.6±2.2	87.1
Eltan	35.6	23.1	15.8	0.7	9.8	85.0
Stephens	34.3	25.9	15.8	0.6	10.2	86.8
Lewjain	34.5	20.9	15.2	1.1	13.1	84.8
Cashup	34.8	28.7	14.4	1.0	12.7	91.5
Rod	28.7	27.8	14.8	1.0	11.1	83.4
Leaves						
	<u>Cellulose (%)</u>	<u>Hemicellulose (%)</u>	<u>Lignin (%)</u>	<u>Extractives (%)</u>	<u>Ash (%)</u>	<u>Total (%)</u>
Madsen	32.6±6.8	33.4±5.9	20.8±3.8	2.4±0.1	13.4±2.2	102.6
Eltan	23.1	28.8	19.7	2.8	8.7	83.0
Stephens	30.2	26.3	24.0	4.1	13.8	98.5
Lewjain	26.3	28.4	22.9	2.2	12.3	92.1
Cashup	28.5	29.0	24.2	3.1	15.1	99.9
Rod	27.0	30.0	21.1	2.8	11.1	92.0

<sup>1</sup> Cellulose, hemicellulose and lignin contents are not ash-free results.

<sup>2</sup> The Total (%) column includes all five columns to the left.

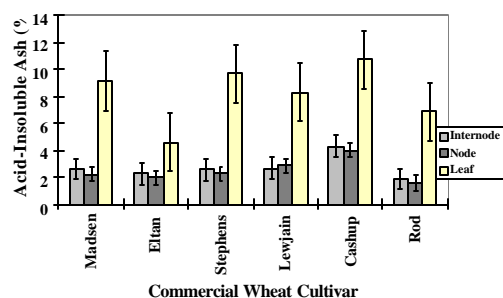
<sup>3</sup> The Cashup cellulose and hemicellulose results may not be reproducible.

<sup>4</sup> Ninety-five percent confidence intervals based on in-field variation.



Error Bars are 95% Confidence Intervals Based on In-Field Variation of Madsen

**Figure 11. Ash Contents**



Error Bars are 95% Confidence Intervals Based on In-Field Variation of Madsen

**Figure 12. Acid-Insoluble Ash Contents**

When comparing commercial cultivars, Cashup had higher silica contents in the nodes and internodes. The leaves in Eltan straw seemed to have less silica than the other major commercial cultivars (Madsen and Stephens). These results suggest that cultivar fractionation may be beneficial if silica content is a limiting factor in a pulp production facility.

Whole straw lignin content have been reported between 16-23% (Table 1). The lignin contents of the different plant sections listed in Table 8 would support total lignin contents in that range. Zhang and coworkers (1990) found the lignin content of the nodal sections (23.22%) to be higher than the leaves (17.48%). Our Moses Lake straw seems to show the opposite trend with the nodes containing similar or less lignin than the leaf sections. The internodal section, which contains the more promising fiber length distribution, contained lignin contents of the same order of magnitude as the leaves and slightly higher than the nodes. While differences in density between nodes and internodes probably are the major influence on pulping kinetics, the lower lignin contents of the nodes may impact the pulping of the nodes.

## 2.0 Wheat Straw Characterization

When determining the metals content of the different fractions of the different cultivars, several of the metals contents were below the detection limit of the ICP. These undetectable compounds included: silver (1 ppm detection limit), arsenic (10 ppm), beryllium (0.5 ppm), bismuth (20 ppm), cadmium (1 ppm), cobalt (1 ppm), lithium (5 ppm), nickel (3 ppm), lead (10 ppm), antimony (10 ppm), and vanadium (1 ppm). The measurable compounds are listed in Table 9.

The compositions listed in Table 9 are not outside the normal range for plant materials; however, the potassium content is higher than that typical of wood. Although these compounds will not affect the pulping and chemical recovery of wheat straw, potassium will have a negative impact on chemical recovery (Grace, 1985).

**Table 9. Range in Metals Between Cultivars (ppm)**

Chemical Compound	Detection Limit	Internode	Node	Leaf
Aluminum, Al	20	<20-20	<20-20	40-100
Boron, B	20	<20	<20	<20-30
Barium, Ba	1	28-83	39-97	47-86
Calcium, Ca	10	1130-3300	2200-3470	5950-8230
Chromium, Cr	1	<1	<1	<1-3
Copper, Cu	2	3-5	3-13	4-6
Iron, Fe	5	21-87	22-68	88-175
Potassium, K	1000	13000-34000	20000-65000	920-1710
Magnesium, Mg	10	500-2970	930-2770	2000-2790
Manganese, Mn	0.5	10.4-25.1	9.3-27.2	34.9-128
Molybdenum, Mo	1	<1 - 2	1-2	<1 - 1
Sodium, Na	50	60-260	20-1570	50-130
Phosphorus, P	20	330-1030	350-1020	920-1710
Tin, Sn	5	<5-6	<5-7	<5-7
Strontium, Sr	0.5	5.8-15.9	9.6-18.8	22.1-37.8
Zinc, Zn	1	7-24	12-25	15-24

While not all of the chemical components of the wheat have been accounted for, the chemical composition of the Moses Lake grown wheat was comparable to other reported values save the extractives values which may be mistakenly low with these samples. The silica content of the leaves were higher than that of the nodes and internodes and some commercial cultivars had different silica distributions than others. Thus, if silica reduction is a priority, removal of the leaves or selective cultivar purchasing may be beneficial.

### 3.0 Pulping and Bleaching

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During early discussions between cooperators in the project, we were requested to consider methods for upgrading straw quality by minimizing the amount of node materials. Elimination of nodes during collection and storage steps would require modification of harvesting equipment to mechanically separate nodes from stem materials. Study and engineering of such a system was beyond the scope of this work; therefore, the focus on pulp upgrading was limited to the pulping system.

The denser nodal material tends to resist penetration by pulping chemical so pulping conditions could be tailored to maximize delignification of stem material leaving nodes largely intact. These larger particles could be separated from the single fibers which originate from the completely pulped stem using conventional screening equipment. Of course, in the process most fine material associated with the nodes and some related silica would be purged from the pulping system presumably upgrading paper quality and eliminating some silica from the recovery system. The penalty of such a system would be economic, primarily in the form of purchased and pulped but unused, oversize rejects materials.

In this project, two types of pulping conditions were used. The first involved a direct, steam-heated cook mode with direct steaming and low water content. As a result, the pulping chemical concentrations were relatively high permitting a short pulping time. With the short reaction times, the denser, poorly impregnated nodes survived the pulping intact as described above. The conditions in these experiments simulate some types of commercial digesters often used for pulping nonwood plant materials.

Later discussions between the cooperators indicated a greater interest in fuller utilization of the purchased plant material including the denser nodes. Consequently, liquid phase pulping was done using larger amounts of water to permit circulation of the pulping liquor through the chopped, compacted plant material in the digester and an external heat exchanger loop was used for indirect heating. This pulping configuration produces more uniform impregnation into the plant material. However, to maintain reasonable pulping times, the total chemical charge was increased to match the increased water and maintain adequate alkali concentrations during the cook. The net result of these modified conditions includes reduction of reject quantities to less than 1%. The condition in these liquid phase cooks also simulate several commercial digester systems.

Bleached straw fibers are good raw material in blends with wood fibers for printing papers. In general the unbleached pulp lignin content should be below about 2.5% (on OD pulp) which is

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## 3.0 Pulping and Bleaching

equivalent to a kappa number of about 18 to 20 if bleaching is preceded by an oxygen stage. In the absence of oxygen and with a total chlorine free (TCF) bleaching sequence the pulp kappa should fall in the range of 10-14 to utilize economical amounts of bleaching agents. Commercial pulping equipment incorporates features to promote impregnation of the plant material by pulping chemicals. Usually presteaming removes some of the water-repelling surface wax layers which predisposes the plant material to imbibe water and pulping chemicals. High pressure feeding equipment can promote more uniform dispersion of chemicals in the plant stems. Vapor phase digesters directly apply steam to complete the pulping reactions. This type of equipment utilizes lower amounts of water so low chemical charges still produce relatively high concentrations and fast reactions. However, any non-uniformity in water or chemical impregnation will result in some partially reacted regions and in production of higher amounts of high lignin rejects. By contrast, liquid phase pulping heats the raw material by circulating liquid through an external steam heated heat exchanger and percolating into the raw material within the digester body.

Some commercial digesters such as the Pandia contains features of both types. The early tubes are largely vapor phase (high consistency) while direct steaming in the later tubes produce condensate and conditions approaching liquid phase. Pulping experiments in the project included vapor and liquid phase conditions. Furthermore, the work was limited to alkaline conditions using sodium hydroxide to support Domtar process studies. Anthraquinone (AQ) pulping additives were incorporated to increase the soda pulping rates.

### 3.1 Vapor Phase Soda/ AQ Pulping

Preliminary experiments showed that presteaming conditions can have a large impact on vapor phase pulping results. Typical trends are shown in Table 10 and in Figure 13 for presteaming times of 15, 30 and 50 minutes. For example, extending the presteaming over those times at 140° C decreases 10 cut screen rejects at all AA charges and H Factors. Generally, the short presteaming times will result in 10 to 15% rejects when pulping at 6 to 12% AA charges. Conversely, the longest presteaming time produces about 1 to 5% rejects at from 400 to 600 H Factor and AA charges greater than about nine percent.

Clearly, manipulation of presteaming, H Factor, and AA charge can control the reject content. In general, rejects may originate from two sources: unseparated fiber bundles and unpulped stem nodes. We want to minimize the former since the bundles contain useful paper making substance. Generally we want to maximize rejection of stem nodes since those morphological plant structures contain fewer tracheids and have more ash and fine plant material. Both ash and fines are detrimental to papermaking. The material contained in rejects at levels below about

## 3.0 Pulping and Bleaching

5% (on OD straw) contain mostly unpulped nodes. A mill process designed to purge nodes could opt for approximately that reject level. A full optimization of conditions to reject nodes and to minimize silica and fines was beyond the scope of this project. However, AA charges of about 8.5 to 10 % at 50 minutes presteaming and 450 to 550 H Factor will probably produce reject levels of 3%  $\pm$  2 percent. More severe conditions will likely increase silica and fines in the pulp and decrease paper properties.

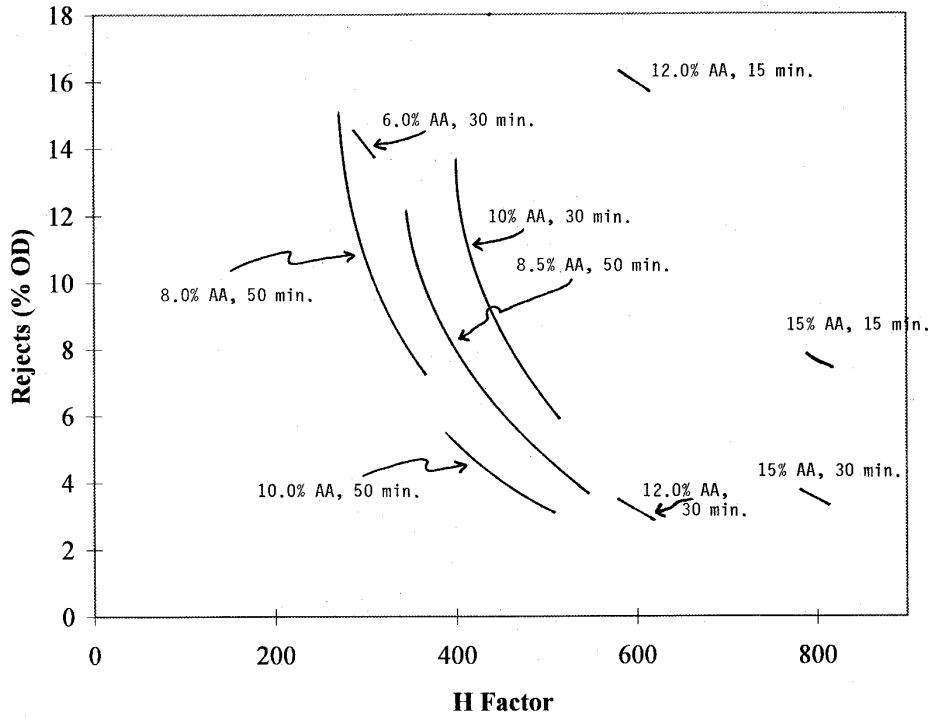
**Table 10. Soda/AQ Vapor Phase Pulping Results\***

Cook	Presteam Time (min.)	A.A. % (on OD straw)	H factor	Rejects, % (on OD straw)	Screen Yield, % (on OD Straw)	Total Yield, % (on OD straw)	Kappa
1	15	15	800	7.6	55.0	62.6	11.9
2	15	12	600	16.0	57.0	72.9	21.7
3	30	15	800	3.5	42.7	46.1	10.2
4	50	12	600	3.1	48.8	51.9	13.0
5	50	6	300	14.1	44.0	58.1	49.5
6	50	8	320	10.1	45.7	55.8	35.2
7	50	10	500	7.1	48.5	55.6	19.0
8	50	10	400	13.3	47.9	61.2	30.8
9	50	10	500	5.3	45.7	51.0	17.9
10	50	10	400	13.9	53.5	67.3	43.4
11	50	8	350	7.6	43.0	50.6	29.0
12	50	8	280	10.8	41.0	51.8	42.7
13	50	8	350	8.4	45.9	54.3	26.8
14	50	8	280	15.1	43.7	58.8	41.2
15	50	8.5	350	12.0	45.8	57.8	37.8
16	50	8.5	400	8.5	45.4	53.9	34.7
17	50	8.5	400	6.9	42.5	49.4	25.4
18	50	8.5	500	4.7	44.6	49.3	26.1
19	50	10	500	0.9	43.5	44.4	10.4
20	50	10	500	3.1	42.5	45.6	10.4
21	50	10	400	5.6	47.0	52.6	14.3
22	50	10	400	4.3	42.6	41.9	11.9
25	50	10	500	3.0	41.2	44.1	13.1
26	50	10	500	3.7	41.6	45.3	13.8
27	50	10	500	6.2	41.8	48.0	17.5
28	50	10	500	3.8	42.6	46.4	13.8
29	50	10	500	5.3	44.3	49.6	18.9
30	50	10	500	2.9	43.8	46.7	16.0

\* Three minute temperature rise and 20 minutes at 170 is equivalent to about 350 H Factor

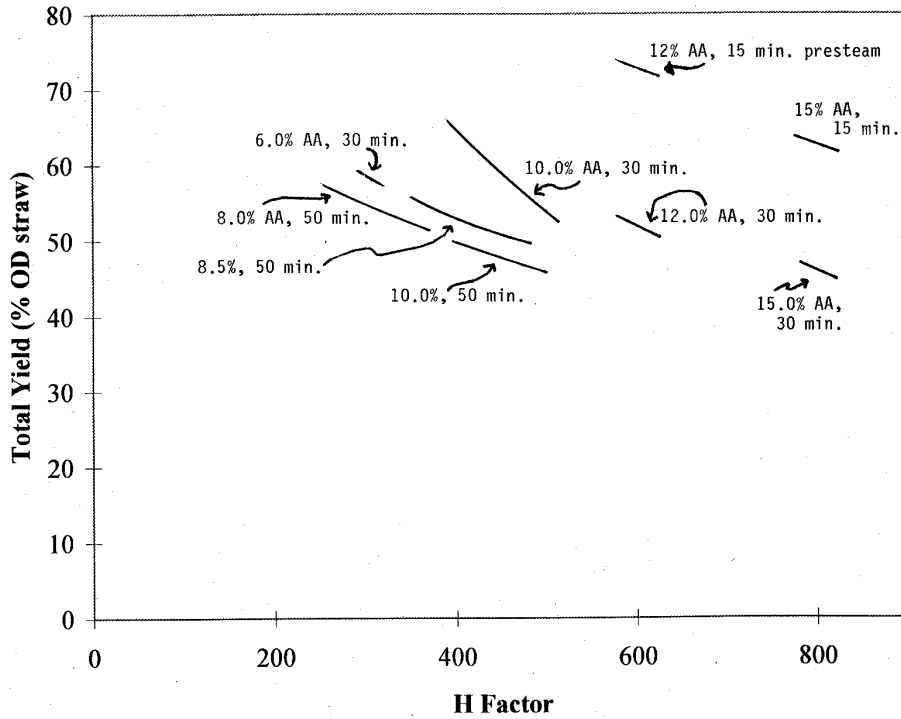
\* 0.05% AQ on OD Straw

### 3.0 Pulping and Bleaching



**Figure 13. Rejects as a Function of H-Factor  
Effect of AA and presteam time; 10 cut screen)**

**Figure 14. Total Yield as a Function of H-Factor**



### 3.0 Pulping and Bleaching

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Results in Figure 14 generally show that total yield drops with longer presteaming and with higher active alkali and H Factor. Clearly, short presteaming times will lead to total yields from 55 to about 75% at 6 to 15% AA and H Factors of 350 to 800. As shown above, the rejects will be high. Conversely, increasing presteaming time to 50 minutes and pulping at 10% AA and 500 H Factor will reduce total yield by 5 to 10 units. AA charges below about 9% will produce high rejects and high accept kappa. AA charges of 12 to 15% will produce low rejects and total yields of 45 to 50 percent. However, the higher AA may decrease the pulp properties. Presteaming and pulping conditions are coupled. The choice of conditions will follow these guidelines with local mill economics imposed.

Figure 15 shows that kappa number of the accept pulps (10 cut screen) also exhibit strong dependence on the same pulping variables. For example, pulps produced by 50 minutes presteaming, 10% AA, and 400 to 500 H Factor have 10 to about 18 kappa number. Shortening the presteaming to 30 minutes will increase kappa number by 10 to 25 kappa units over the same H Factor range. Bleaching of straw pulps by simple, three stage sequences will probably begin with unbleached pulp at from 15 to 20 kappa number. Therefore, short presteaming times and AA charges less than 9 to 10% will be unacceptable because kappa numbers will exceed this range.

Higher H Factor and AA charges (500 to 800 and 12 to 15%, respectively) will produce lower kappa numbers. But, pulp properties and bleached yields will probably suffer. So the major part of this project to date has focused on bleaching of pulps falling in the range of 15 to 18 kappa. The bleaching work described below utilized a blend of cooks 25 to 30 prepared by 50 minute presteaming, 10% AA, and 500 H Factor with an unbleached kappa of 16.5, total yield of 46.7, and screened yield of 42.6% (on OD straw).

Results in Figure 16 compare total and screened yield over those conditions most likely of commercial interest. Results at lower and higher alkali charges are eliminated for reasons discussed above.

The equipment available at the University of Washington for vapor phase cooks clearly produced deficiencies in liquor impregnation which resulted in higher reject levels than desirable. Commercial digesters such as the Pandia employ more efficient impregnation systems than possible in laboratory equipment. Consequently, shorter, less damaging presteaming coupled with the optimum alkali charges and H Factor mentioned above will probably produce lower rejects and bleachable kappa number.

### 3.2 Liquid Phase Soda/AQ Pulping

If lower rejects are required, liquid phase pulping may be more desirable. Liquid phase pulping conditions more clearly mimic digesters which process wood chips and in some type of digester designs may be applied to straw material. However, the bulky, more porous straw requires higher liquid/plant solid (L/W) values to maintain liquid circulation. In continuous straw digesters the L/W may be about 6/1 while in smaller laboratory digesters the value is usually 8/1. To maintain comparable pulping rates at higher liquid ratios the sodium hydroxide charge must be proportionately higher than used in the vapor phase cooks. Pulping results are summarized in Table 11.

### 3.0 Pulping and Bleaching

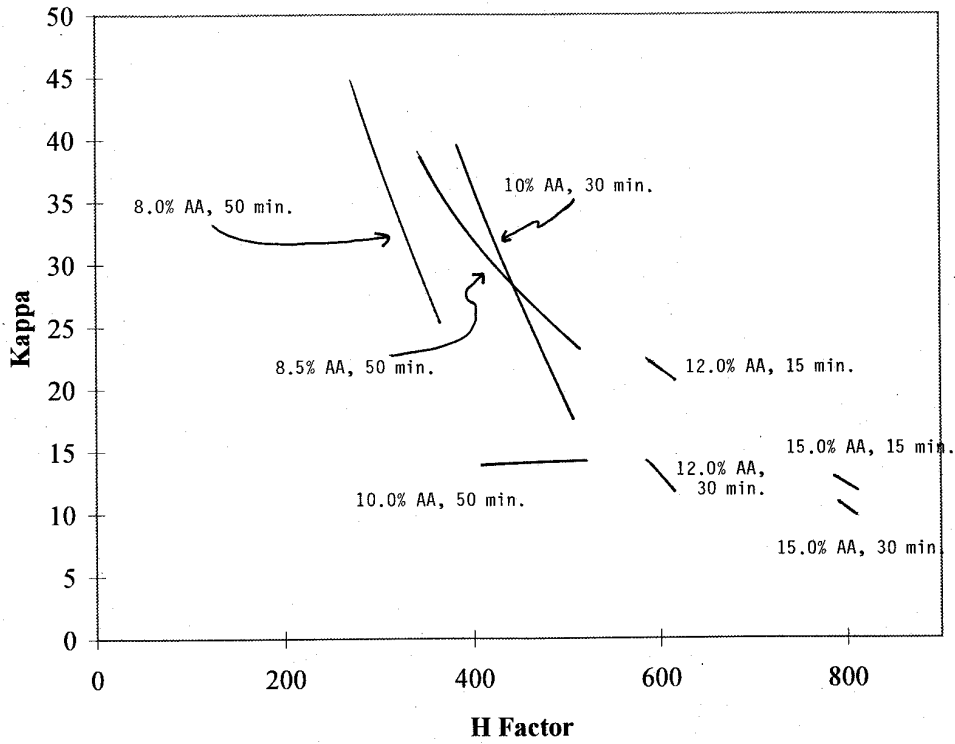


Figure 15. Accept Kappa Number as a Function of H-Factor (10 cut screen)

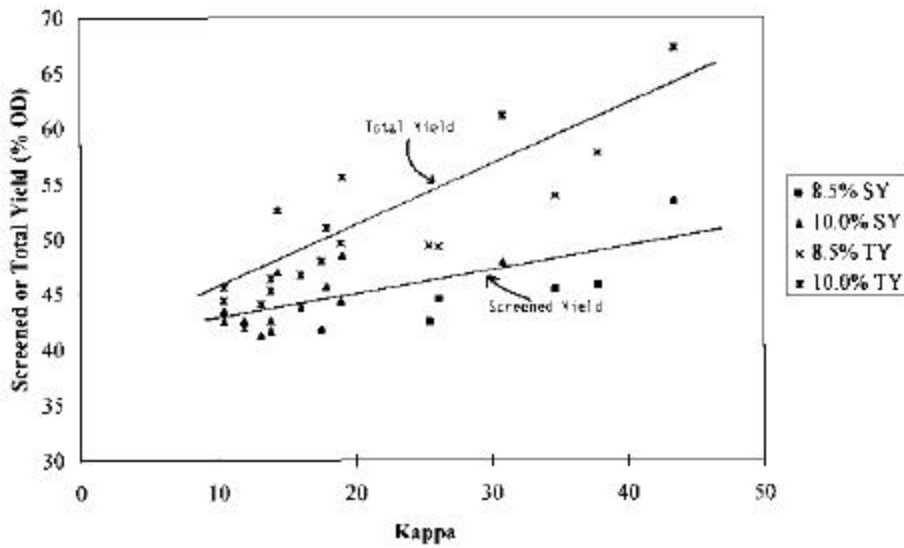


Figure 16. Screened and Total Yields

## 3.0 Pulping and Bleaching

**Table 11. Soda/AQ Liquid Phase Pulping Results\***

Cook	Presteam Time (min.) (on OD straw)	A.A. % (on OD straw)	H factor	Rejects, % (on OD straw)	Screen Yield, % (on OD Straw)	Total Yield, % (on OD straw)	Kappa
31	5	16	1864	0.3	48.1	48.4	18.6
32	5	18.7	2197	0.1	43.7	43.8	10.3
33	5	18.7	2197	0.1	43.7	43.8	10.3
34	5	18.7	2197	0.1	43.7	43.8	10.3
35	5	17.2	1964	0.2	47.4	47.6	14.5
36	5	17.2	1964	0.2	47.9	48.1	14.5

\* presteam at 100°C

\* 8/1 liquor/wood ratio

\* 1 hour temperature rise and 2 hours at 170°C is equivalent to H Factor of 1964 assuming activation energy of 32 kcal/mole

\* 0.05% AQ on OD straw

With liquid phase pulping the combination of longer pulping time and the larger volume of liquid results in more uniform chemical impregnation of the straw than possible in the shorter vapor phase cooks. Consequently, reject quantities are considerably lower. One might expect that complete pulping with lower rejects and higher accepts may produce greater yields than in vapor phase cooks. However, the longer pulping times and larger proportion of liquid probably also promote greater dissolution of hemicelluloses in the liquid phase cooks. As a result, the rejects quantities are lower and total pulp yields are slightly lower than obtained in vapor phase cooks at the same kappa number.

Selection of the pulping conditions will depend on the digester type, the pulp processing design and economics, and on the raw material costs.

### 3.3 Soda/Oxygen Pulping

The combination of caustic and oxygen acts as an effective delignifying agent for a range of plant materials including cereal grain straw. In the present project this combination has been studied in two ways. First, soda/oxygen pulping of straw using vapor phase heating has produced bleachable pulps as described below. Second, several of the low kappa pulps have been bleached as described later using an oxygen bleach stage.

While oxygen stages increase pulp line capital costs, many designs include this technology because of operating or environmental cost benefits. A recent study (Chen, 1996) suggests that combinations of soda and oxygen may cause silica which was dissolved from the straw in early stages of pulping to redeposit onto the pulp as a result of recirculation of the oxygen stage wash filtrate. Such a system could reduce silica contamination of the black liquor by purging the silica as a deposit on the pulp. Limited experiments were done in the present work to determine the

## **3.0 Pulping and Bleaching**

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effect of alkali charge and oxygen conditions on the kappa number and pulp yield. The soda/oxygen pulping

## 3.0 Pulping and Bleaching

produced unbleached pulps falling in the range 12 to 22 kappa. The conditions shown in Table 12 are mild compared to soda/AQ pulping.

**Table 12. Soda/Oxygen Pulping\***

AA, % (on OD straw)	Rejects, % (on OD straw)	Screened Yield, % (on OD straw)	Total Yield, % (on OD straw)	Kappa
4	39.1	22.3	61.4	44
6	28.7	30.6	59.3	31
8	25.4	31.1	56.0	24
10	15.0	40.8	55.8	16
12	4.4	48.4	52.8	12

\* Cooking Conditions

- Presteam for 50 minutes at 140°C
- AQ at 0.05% on OD straw
- 1 hour soak at 90°C and 1 hour at 120°C and 75 psig O<sub>2</sub>

All cooks were made using straw presteamed 50 minutes at 140° C. The straw was heated for one hour at 90° C following impregnation with 4 to 12% alkali. For each cook the digester was then pressurized to 75 psig with oxygen and the temperature held at 120° C for one hour. The results in Table 12 suggest that under these conditions 10 to 12 % AA will produce pulp at 12 to 18 kappa, 48 to 50% screened yield and 52 to 54% total yield. Despite the prolonged steaming times which may dissolve some hemicellulose, these conditions produce significant yield improvements compared to the soda/AQ pulping.

However, alkali consumption may increase 10 to 20%, relative to soda/AQ pulping, probably as a result of neutralization of acids generated by the oxidation of plant material during the pulping.

### 3.4 Bleaching Vapor Phase Pulps

Each of the straw pulps were bleached by several sequences to compare bleach response and physical properties. The target brightness for the first round of tests was 85 to 87. Bleach conditions and brightnesses are summarized in Table 13. The common sequence for all pulps was DEoD. For soda/AQ the D<sub>1</sub> charge was based on a kappa factor of 0.24 to 0.26. The kappa factor was lowered to 0.24 for soda/oxygen pulp because the mild pulping conditions may lead to easier bleaching. The soda/AQ pulps were also prebleached with an oxygen stage at conditions selected for about 50% delignification. The lower kappa soda/oxygen pulp was bleached only with the three stage sequences shown.

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## 3.0 Pulping and Bleaching

First, compare the three pulps in terms of DE<sub>o</sub>D response. The soda/AQ pulp reached 81.4 brightness under the conditions shown. Note that the chemical charges and conditions were not optimized for all stages. Notice that the soda/oxygen pulp bleached by DE<sub>o</sub>D reaches about the same brightness(80.2) compared to the soda/AQ when chemical charges had been adjusted to reflect the differences in unbleached kappa. A rigorous comparison must await the optimization based on two pulps with close unbleached kappa numbers. However, this comparison does not indicate great differences in the bleachability of the soda/AQ and the soda/oxygen pulps.

Refer now to the sequence ODE<sub>o</sub>D applied to the soda/AQ pulp. The former readily delignifies in the O stage to 4.7 kappa (72% lignin removal). The final brightness was 78.4 when using a kappa factor of 0.24 in the D<sub>1</sub> stage and 0.4% ClO<sub>2</sub> in the D<sub>2</sub> stage. Despite the extensive O stage delignification, clearly higher D charges will be required for full bleaching.

### 3.5 Bleaching Liquid Phase Soda/AQ Pulp

Liquid phase, soda AQ pulping offers the greatest commercial interest to Domtar since those process conditions minimize the pulp rejects and result in kappa number of 10 to 14. Pulps at these lignin contents should readily reach brightness values of 86-88 in three bleaching stages. Consequently, pulps numbered 32-34 in Table 11 were bleached by a DE<sub>o</sub>D sequence to the above brightness range. The bleaching results are summarized in Table 14 and the composite pulp reached a brightness of 86.4. This pulp was used, as described later, alone and in blends to produce paper handsheets for testing purposes.

### 3.0 Pulping and Bleaching

**Table13. Soda/AQ Vapor Phase Pulp Bleaching Results**

Pulp	Initial Kappa	Bleaching Sequence	O <sub>2</sub> Stage (100 °C, 115 psig, 90 min, 3.1% NaOH)			D <sub>1</sub> Stage (60 °C, 30 min, 4% cons.)			E <sub>0</sub> Stage (65 °C, 45 min. 35 psig, 10% Consis. 3.1% NaOH)		D <sub>2</sub> Stage (80 °C, 120 min, 10% consis.)			Final Brightness	
			pH out	Kappa Out	Brightness Out	Kappa Factor	Resid. pH	Consump. (%)	pH out	Brightness Out	Charge (%)	Resid pH	Consump. (%)		Brightness Out
Soda AQ	16	DE <sub>0</sub> D				0.26	3.5	44%	11.8	n/a	1.1	3.5	98%	81.4	81.4
	16	ODE <sub>0</sub> D	10.2	4.7	58.4	0.24	7.0	100%	12.1	77.5	0.44	6	100%	78.4	78.4
Soda O <sub>2</sub>	12	DE <sub>0</sub> D				0.24	4.3	100%	11.9	73.7	1.21	2.6	92%	80.1	80.1

**Table 14. Soda/AQ Liquid Phase Pulp Bleaching Results**

Pulp	Initial Kappa	Bleaching Sequence	D <sub>0</sub> Charge			E <sub>0</sub> Charge		D <sub>1</sub> Charge 1.5%			Final
			KF	Residual pH	Consumption (%)	pH out	R <sub>∞</sub>	Residual pH	Consumption (%)	R <sub>∞</sub>	R <sub>∞</sub>
Soda AQ	10.3	DE <sub>0</sub> D	0.3	2.4	93.9	12	73.5	2	67.4	86.4	86.4

## 4.0 Handsheet Testing

Handsheet papers were prepared from three types of pulps: a) unbleached, vapor phase pulps, b) partially bleached ( $80 \pm 2$  brightness), vapor phase pulps, c) fully bleached (86.4 brightness), liquid phase pulps. As already mentioned, the liquid phase pulps were prepared at lower kappa and with minimum rejects and were therefore of greatest interest to Domtar. Consequently, bleached, liquid phase pulps (86.4 brightness) were blended with Domtar Crystal pulp.

### 4.1 Vapor Phase Pulps

Thin straw fibers easily refine to low Canadian Standard Freeness (CSF). These trends are confirmed for the present pulps in Table 15.

**Table 15. Unbleached Handsheets -- Vapor Phase Pulps**

Pulp	Unbleached Kappa	PFI Rev.	CSF (mL)	Basis Weight ( $g/m^2$ )	Apparent Density ( $g/cm^3$ )	Tensile Index (N m/g)	Tear Index 1-ply ( $mN m^2/g$ )	Brightness (% ISO)
NaOH/AQ	16	0	450	59.2	0.578	81.7	6.43	23.5
		400	320	63.3	0.619	86.7	5.79	24.3
		1000	240	66.2	0.708	82.0	5.55	27.2
NaOH/O <sub>2</sub>	12	0	350	61.1	0.769	69.6	7.42	36.1

Furthermore, the apparent density of these pulps range from about  $1/2$  to  $3/4 g/m^3$  also as a result of the large fraction of small fibers and fiber fragments. The high bond area associated with the high paper density results in relatively high tensile index despite the predominance of short fibers in wheat straw. Conversely, the tear index is lower than most wood pulps, again as a result of the low average fiber length.

Notice that soda/O<sub>2</sub> pulps had four kappa unit lower than soda/AQ. The higher density probably results from the more flexible, lower lignin content fibers. Tensile strength losses presumably come from the higher alkali charges required in that process chemistry and/or pulp damage associated with pulping to lower lignin levels using oxygen. Of course, the oxygen treatment tended to raise the pulp brightness relative to the soda/AQ pulps.

Partial bleaching to brightness levels of  $80 \pm 2$  units resulted in a general increase in apparent density as shown in Table 16.

**Table 16. Bleached Handsheets -- Vapor Phase Pulps**

Pulp	Bleaching Sequence	PFI Rev.	CSF (mL)	Basis Weight (g/m <sup>2</sup> )	Apparent Density (g/cm <sup>3</sup> )	Tensile Index (N m/g)	Tear Index 1-ply (mN m <sup>2</sup> /g)	Brightness (% ISO)	Opacity (ISO)
NaOH/AQ	DE <sub>0</sub> D	0	380	66.7	0.741	85.3	7.18	81.4	73.0
	DE <sub>0</sub> D	400	270	64.9	0.792	62.5	7.87	76.9	70.8
	ODE <sub>0</sub> D	0	n/a	59.6	0.724	76.8	6.91	78.4	73.9
NaOH/O <sub>2</sub>	DE <sub>0</sub> D	0	315	59.8	0.817	76.6	6.76	80.1	69.3

Bleaching typically produces more flexible fibers so density increases. The DE<sub>0</sub>D sequence did not contribute much loss in tensile relative to unbleached pulps. However, insertion of the strong oxygen stage (O) in two sequences resulted in a clear drop in tensile relative to the DE<sub>0</sub>D sequence. The combined detriments of high capital oxygen stage costs and the strength losses strongly favor the DE<sub>0</sub>D sequence.

### 4.2 Liquid Phase Pulp

Liquid phase soda/AQ pulps were evaluated more completely to support Domtar interests. These pulps were converted to handsheets alone and in blends with Domtar supplied Crystal pulp. To help interpret paper properties, each pulp was analyzed in triplicate for fiber properties shown in Table 17 and in Figure 17.

**Table 17. Kajaani Fiber Length and Coarseness**

Sample	Numerical Average (mm)	L. Weighted Avg. (mm)	W. Weighted Average (mm)	Coarseness (mg/m)
Crystal-1	0.49	1.39	2.37	0.075
Crystal-2	0.48	1.39	2.39	0.076
Crystal-3	0.49	1.41	2.39	0.074
SAQ Wheat-1	0.35	0.79	1.30	0.046
SAQ Wheat-2	0.35	0.79	1.30	0.043
SAQ Wheat-3	0.35	0.79	1.30	0.047

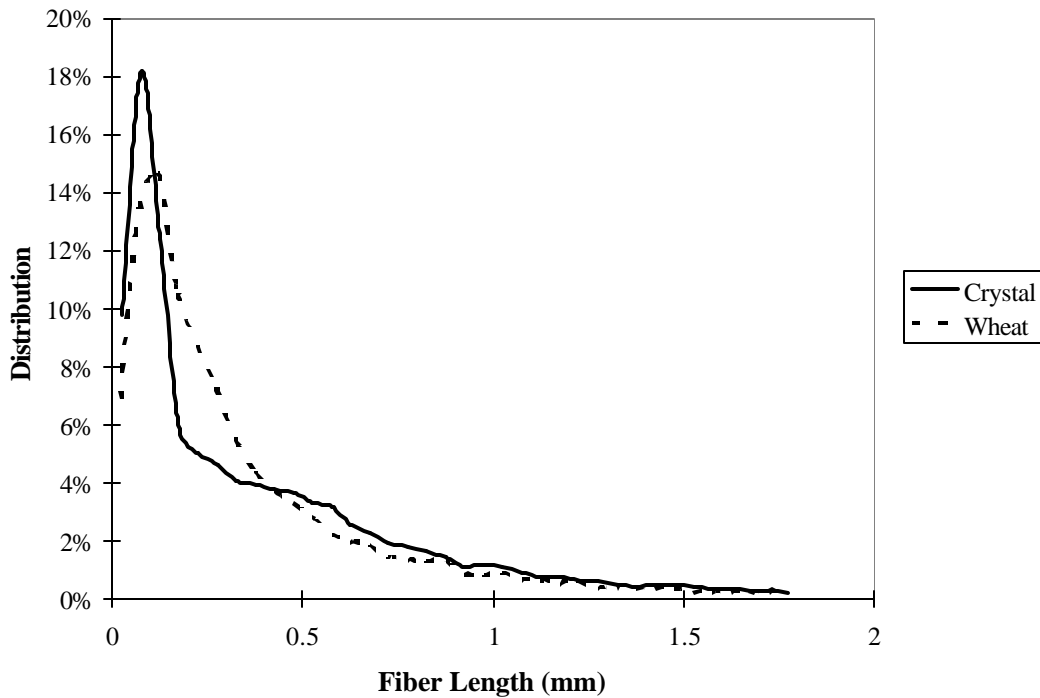


Figure 17. Comparison of fiber length distributions.

Old corrugated containers (OCC), the parent source of Crystal pulp, contain blends of hardwood and softwood from kraft and semichemical processes, so the fiber length depends on the composition of the raw material and on fiber damage incurred during OCC processing. The broad range of pulp fiber lengths is displayed in Figure 17. Since Crystal pulp contains substantial short fiber fragments the arithmetic average amounts to about 0.49 mm. Notice that the average is slightly greater than the straw pulp. Also notice that the number average straw pulp fiber length agrees well with the whole plant number average length shown in Table 6. Finally, the pulp length weighted average length is slightly greater than the whole plant value. How could that be possible? During pulp processing, some fines were probably dissolved leading to the larger calculated weighted average shown in Table 17 relative to Table 6.

Since paper properties depend heavily on a presence in the furnish of some long fibers, papermakers prefer to forecast paper properties from the calculated length weighted or mass weighted averages. The small amounts of longer fiber fractions in the Crystal pulp lead to significantly higher weighted averages relative to the straw pulp. While the difference in quantity of longer fiber appears small in Figure 17, it is significant enough to cause some differences in properties of paper derived from the two types of pulp.

## 4.0 Handsheet Testing

Notice the coarseness of Crystal pulp exceeds the straw pulp by nearly a factor of two. Thicker walled hardwood and softwood fibers in Crystal pulp result in significantly higher mass per unit length (coarseness) than in straw pulp. Both the length and coarseness differences will favor the Crystal pulp in terms of strength properties.

Pulp viscosity often is used to measure fiber damage during bleaching and to forecast paper properties. The values shown in Table 18 are averages of triplicate measurements.

**Table 18. Viscosity (g/cm\*sec)**

unbleached SAQ:	0.32	(0.007)
bleached SAQ:	0.20	(0.15)

values in parentheses indicate 95% confidence

Unbleached straw pulps typically have viscosity from 0.3 to 0.35 g/cm sec for a range of sources and pulping processes (Misra, 1987). Viscosity changes in bleaching are related to chemical-induced shortening of the cellulose molecules comprising fiber cell walls. Bleaching-induced viscosity losses depend strongly on the bleach sequences and on individual stage conditions. The bleached-pulp viscosity in Table 18 falls at the high end reported in the literature (Misra, 1987). Clearly, the combination of pulping and bleaching conditions needed to produce fully bleached soda AQ (SAQ) pulps in this study caused relatively mild fiber damage.

For a sequence of blends shown in Table 19 ranging from pure straw pulp to pure crystal pulp, the paper density drops about 20 percent. The shorter, more slender straw pulp will tend to compact in a dry sheet to higher density than the longer fiber, thicker walled crystal pulp.

**Table 19. Domtar Crystal Pulp / SAQ Wheat Straw Pulp Study**

Sample	Brightness	Caliper (mm)	Basis Wt. (g/m <sup>2</sup> )	Density (g/cm <sup>3</sup> )	Opacity	Tensile Index (Nm/g)	Tear Index* (mN*m <sup>2</sup> /g)	Burst Index (kPa*m <sup>2</sup> /g)	Porosity (sec/100ml)
100% SAQ & 0% Crystal	86.4	0.08	58.7	0.75	71.1	55.0	6.7	4.8	205
75% SAQ & 25% Crystal	87.6	0.09	60.8	0.71	71.6	57.7	7.9	4.9	132
50% SAQ & 50% Crystal	86.8	0.09	60.0	0.68	72.0	58.8	9.4	5.3	103
25% SAQ & 75% Crystal	86.3	0.09	61.2	0.65	72.4	59.3	9.9	5.4	77
0% SAQ & 100% Crystal	85.4	0.10	60.3	0.61	72.9	49.4	11.3	5.4	34

\* single-ply tear

The mixture of fiber lengths (see Figure 17) in the higher density and better bonded straw pulp produces about 10% higher tensile strength than the pure crystal pulp. However, the presence of more long fibers in the latter results in about 80% higher tear strength than in pure straw papers. Only small differences are apparent in burst strength. Blends of the two pulps fall proportionately between the limiting cases.

The presence of more short fibers and fiber fragments in the straw pulp, which result in higher paper density, produces a highly bonded structure with low porosity (longer time /100 ml of air passage).

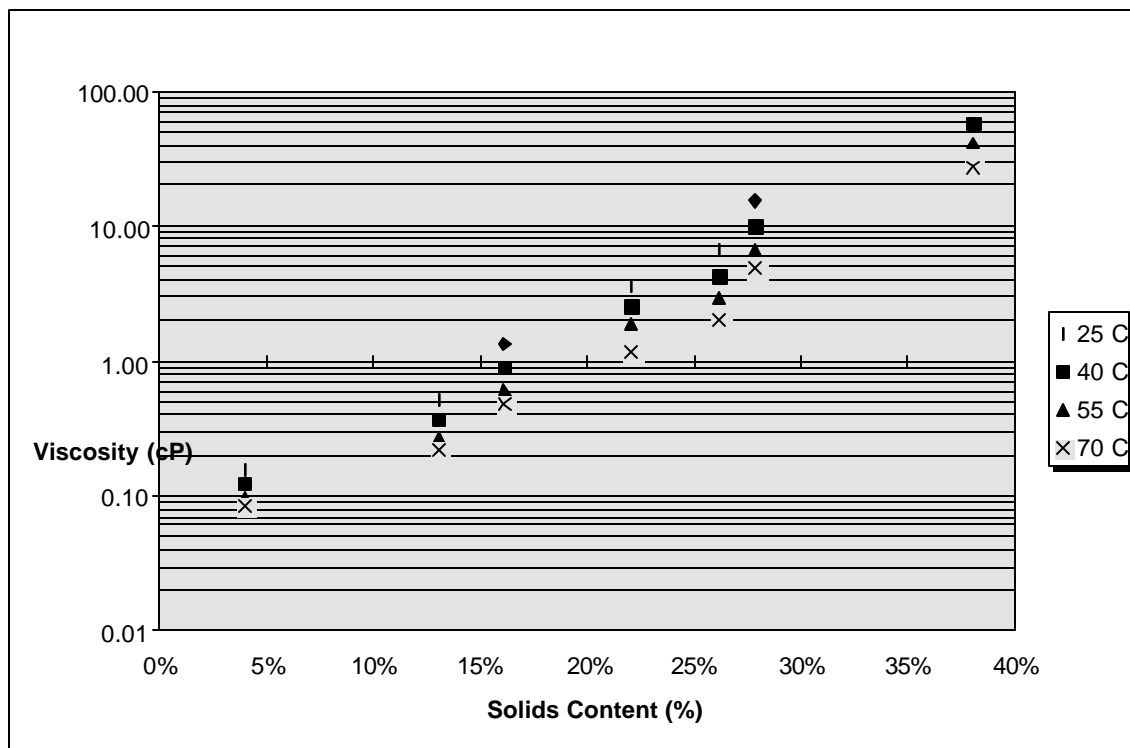
All these physical properties are similar in magnitude to reported results for wheat straw (Misra, 1987). As expected, Crystal pulp and straw pulps have some differences in fiber morphology and paper properties of the pure furnishes. Blends of these pulps offer opportunities for achieving combinations of physical properties and porosity for manufacturing communication papers.

Black liquor processing usually includes evaporation, concentration and combustion steps; flow and process designs require information on chemical and physical properties of the liquor. Design of evaporators and associated flow systems requires information on viscosity over a range of solids content and temperatures. Heating values are incorporated in design and performance calculations for combustion recovery systems. Finally, metal elemental analysis permits forecasts of potential harmful deposits on the heat transfer surfaces in evaporators and combustion equipment.

### 5.1 Soda/AQ Liquor Viscosities

Soda/AQ (SAQ) liquors produced in liquid phase cooks 31, 32, 33 (refer to Table 11) were analyzed in terms of solids/viscosity, inorganic/organic ratio, non-process elements evident, and heating value to help project possible effects on commercial liquor handling steps. All measurements were made in duplicate with average values reported.

SAQ liquor was concentrated to solids contents shown in Figure 18 and the capillary viscometry values were measured at the temperatures shown.



**Figure 18. Viscosity of soda/AQ black liquor at various solids contents and temperatures.**

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## 5.0 Black Liquor Properties

The increase in viscosity with solids content plotted in semilog scale follows typical trends for alkaline and acid liquor from wood pulping (Venkatesh, 1985). However, straw liquor viscosities are significantly higher than wood based liquor over the range of temperatures and solids content shown. For example, kraft liquor viscosity at 70° C and 40% solids will range from 8 to 10 cP depending on wood species and pulp yield. At the same conditions, this straw liquor has viscosity of 27.9 cP. Presumably this trend toward higher viscosities will remain at solid contents in the range 40-60% which are typical for economic operation of recovery systems. Design of concentration, storage, and combustion systems must reflect these significantly higher values.

### 5.2 Soda/AQ Black Liquor Heating Values

Heating values measured by the ASTM D2015 procedure are listed in Table 20.

**Table 20. Straw Liquor Heating Value**

<u>Sample</u>	<u>HHV Btu/lb</u>
Soda/AQ -1	6250
Soda/AQ -2	6540

While heating value depends on wood species and pulp yield, typical values for kraft pulping of wood range from about 5800 to 6600 Btu/lb (Hough, 1985). Straw pulping conditions and liquor composition vary from wood based systems sufficiently enough to expect some difference in heating value. These pulps were prepared at total alkali charges similar to wood pulping. The straw pulp yield was about 2-3% lower than expected for wood. The measured inorganic/organic ratio in the straw liquor was 0.448 which is slightly lower than wood as a result of greater yield loss and greater quantity of dissolved organic material contained in the liquor. Finally, straw contains a greater proportion of lower heat content carbohydrates than wood. The net effect of these factors leads to the heating values reported in Table 20. They are within the range of reported wood based liquors, but probably lie at the top of the range expected for annual crops.

### 5.3 Soda/AQ Black Liquor Metal Assay

In alkaline pulp mills with liquor burning cycles, trace metal analysis can provide some warning of potential process problems. For example calcium, aluminum, and silica can contribute to the formation of scales on process equipment surfaces. High potassium content may contribute to combustion problems and several cations may participate in smelt water explosions.

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## 5.0 Black Liquor Properties

The concentrations of sixteen elements in Soda/AQ black liquors are shown in Table 20-a. Notice the very high level of potassium which originates from the wheat straw. This level is much higher than occurs in wood-based systems which may contribute to changes in the recovery furnace smelt melting temperature (Grace, 1985, pg. 115). The other elements are present at concentrations within the range expected for wood.

The absolute quantities and the ratios of aluminum and of silica often signal potential problems in the recovery area associated with difficult to remove deposits on heat transfer surfaces. Furthermore, high aluminum and silica will increase viscosity of smelts and promote slag deposits in the smelt area (Grace, 1985, pg. 184). The aluminum and silica concentrations in this soda/AQ black liquor are well within levels reported for wood (Grace, 1985). Particularly, the silica content (171 ppm) is 1/10 to 1/20 of levels reported for pulping of nonwood plants (Misra, 1987; Chen, 1996). However, the various reports are unclear about the process conditions under which the liquor samples were generated. Samples collected in laboratory pulping studies without liquor cycling through a recovery system will likely have significantly lower aluminum and silica content than the liquor collected from a mill with chemical recovery loop. The retention of these species and their concentrations in black will increase substantially as a result of the operation of a recovery system.

While aluminum and silica contents of the present black liquors appear low, the levels will likely be higher in a soda/AQ equipped with recovery loop. Forecast of levels will depend on the particular mill design and degree of closure and such forecasts are beyond the scope of this project. Estimates of maximum acceptable aluminum and silica levels in a mill black liquor depend on the ratio of the two metals, but typically amount to about 400 ppm for each metal (Battan, 1997).

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## 5.0 Black Liquor Properties

**Table 20-a. Metals Analysis of Soda/AQ Black Liquor**

<u>Metal</u>	<u>Amount (µg)</u>
Aluminum	13.8
Boron	18.5
Barium	2.84
Calcium	141
Chromium	0.95
Copper	6.78
Iron	13.64
Magnesium	10.165
Manganese	1.68
Nickel	7.66
Phosphorus	738
Potassium	40530
Selenium	11.64
Silica	171.5
Sodium	77852.5
Sulfur	2180

## 6.0 Conclusions

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1. Separation of leaves and nodes will increase average fiber length.
2. Irrigation produces straw with average fiber length about 0.1 mm (20%) longer than dry land farming.
3. Stem, nodes, and leaves of five cultivars studied contain about 7.5%, 11.5%, and 13% ash, respectively, most of which is silica. The Eltan cultivar has about 3/4 of these quantities for each plant segment.
4. Nodes and leaves (1/2 of plant weight) contain about 2/3 of the silica, so in-field fractionation will only marginally decrease the silica load into the pulp mill.
5. The high plant potassium content appears as high potassium load in the black liquor.
6. Soda/AQ pulping can produce bleachable pulp at 10-12 kappa and about 44% yield.
7. DE<sub>0</sub>D bleaching of the soda/AQ pulp produces about 10% shrinkage for total yield of about 40 percent.
8. Fully bleached straw paper strength alone and in blends with Crystal pulp has tensile and tear strengths comparable to hardwood blends for fine papers.
9. Straw black liquors are 2-3 times more viscous than kraft/wood liquors over the range of 5 to 40% solids and up to 70°C.
10. Straw black liquor heating values fall in the range expected for bleachable grade wood/kraft liquor.
11. Silica and aluminum content of laboratory made straw liquors lies well below literature values reported for straw liquors. The steady state levels of these metal ions in a full sized mill with normal liquor closure would be considerably higher.

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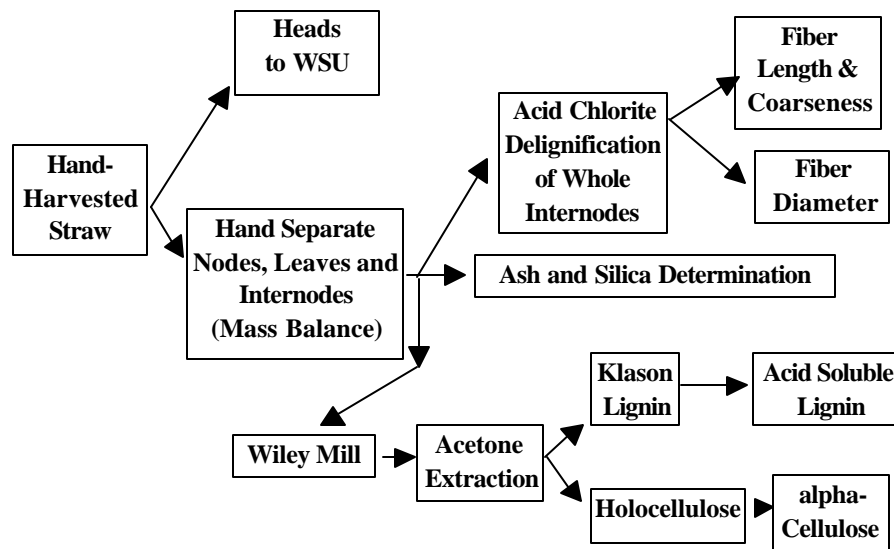
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### **Wheat Straw Characterization**

In Phase 1 of this project, the chemical composition and fiber morphology were compared for six hand-harvested commercial cultivars (Table 1) from Moses Lake, WA. The cultivars were grown using a randomized block experiment with four replications. For each sample, the head of the plant (which contains the grain and chaff) was hand separated and sent to Washington

State University (WSU) for grain yield determinations. A portion of the straw was then fractionated and analyzed. Figure 2 illustrates the analytical steps.



**Figure 2. Flowchart of Experimental Methods**

The leaves, nodes, and internodes were hand separated using scissors. The sheaths were added to the leaf fraction. Ashing was done at 500°C. This ash was used to determine the silica and silicates content, acid insoluble ash, using SCAN C9:62.

Internodes sections were randomly selected and the composite material was acid chlorite delignified using TAPPI Method T-259 om88 adapted for larger quantities. The fiber length distribution and coarseness of the resulting pulp was then determined using a Kajaani FS-200. The fiber diameter distribution was determined optically using an image analysis system linked to a microscope. The image analysis system uses Bioscan's Optimas software. The diameters of all cells were included in this measurement. This measurement technique resulted in large average cell diameters. When only tracheid diameters were measured for one cultivar, average tracheid diameter results were one-third of the average cell diameters and comparable to literature.

The remaining node, leaf, and internode samples were sent through the Wiley Mill with a 1 mm screen. Each sample was then acetone extracted in a Soxlet apparatus for eight cycles. The extractive free samples were then divided into two parts. The Klason lignin content was determined on a portion of the sample using Effland's [1977] adaptation of TAPPI Method T222 os-74. This adaptation has been used successfully by Aoyama and coworkers [1993] on bamboo and by Billa and Monties [1995] on wheat. Acid-soluble lignin was determined using Browning's method [1967] at 205 nm. The Klason lignin and the soluble lignin contents were combined to report the total lignin content for each cultivar. Holocellulose and alpha-cellulose

determinations were also done using Browning's Methods [1967]. Note that none of the holocellulose, alpha-cellulose, and Klason lignin results were corrected for possible ash content.

With the possibility of in-field variation affecting chemical and morphological results, all four field replicates were analyzed for the Madsen cultivar. With the other five commercial cultivars, only the first replicates were tested.

### **Pulping and Bleaching**

#### **Soda AQ Pulping -- Vapor Phase**

In Phase II of this project, machine-harvested, whole Madsen wheat straw was pulped and bleached by various combinations of processes. The process steps are outlined in Figure 19. Notice that soda/AQ and soda/oxygen cooks were preceded by presteaming and chemical impregnation steps to ensure uniform chemical distribution in the plant material before the vapor phase cooks. The vapor phase cooks were made in 10 l digesters shown schematically in Figure 20. Cooking steps and conditions follow the sequence below for an example using 300 g OD straw.

- a. Presteamed straw at about 35% solids content is mixed in a Hobart mixer with 150 ml of alkali/AQ applied with a thin spray over about five minutes of mixing. The resulting solids content is 30 percent.
- b. This straw is tightly compacted in cheese cloth and microwave preheated in two minutes to about 100° C.
- c. The digester is preheated with high pressure steam to 100° C.
- d. The preheated straw bag is suspended in the digester above the predetermined condensate level.
- e. After air purge, the digester and contents are heated and controlled at the target temperature by metering high pressure steam to maintain the appropriate pressure.
- f. Rapid steam relief terminates the cook.

With this procedure, condensate generated in heating the digester vessel accumulates in the bottom of the digester, separate from the cooking straw. Of course, the condensate generated by heating the bag contents remains with the straw and raises the L/W ratio.

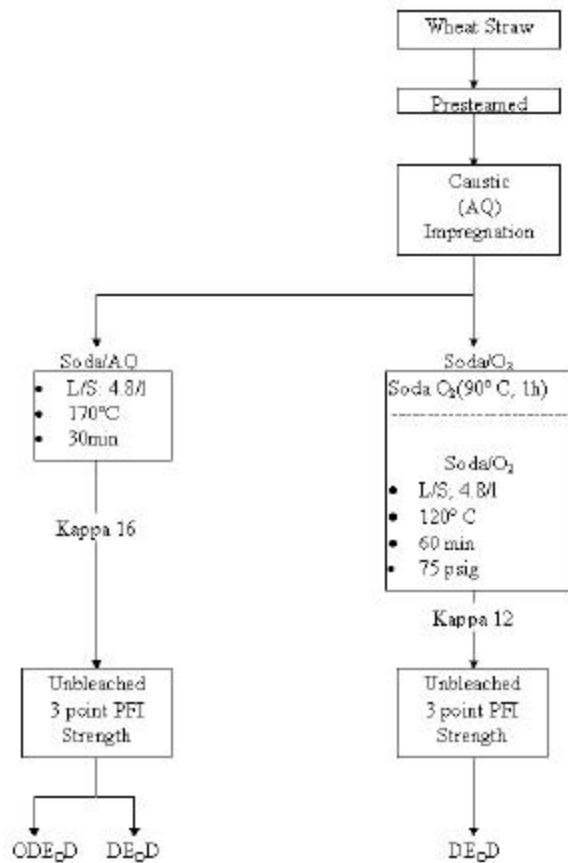
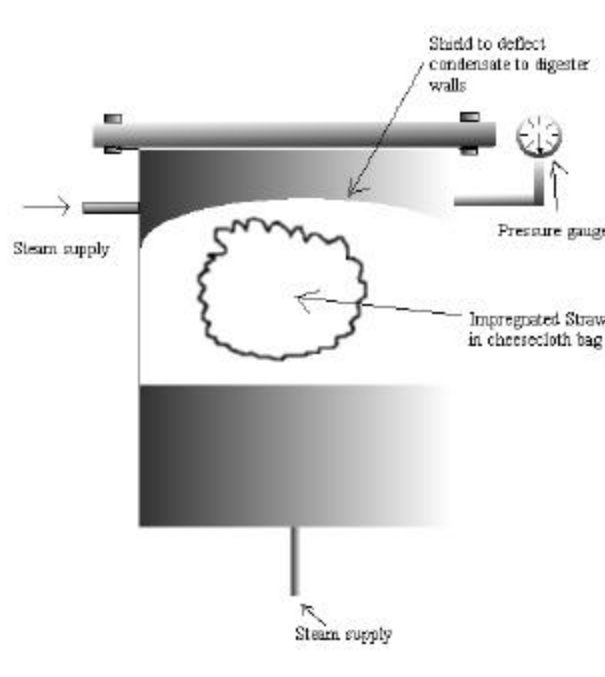


Figure 19. Schematic of Pulping and Bleaching



**Figure 20. Digester**

For example, 300 g (OD) at 30% solids require about 750 g of steam to heat from 100° C to 170° C. This will increase the L/W ratio in the bag to 4.8/1 ( $\approx$ 17% solids) during the cook.

Preliminary experiments with a thermocouple embedded in the center of the straw bag confirmed rapid heat transfer to that location. For example, 300 g straw at 30% solids was heated from 100° C to 170° C in about three minutes by the condensing steam. Consequently, these procedures result in heating the straw mass and associated moisture and pulping chemical to the pulping temperature in a total time of about six minutes. These steps and the changes in straw consistency roughly simulate conditions in a Pandia digester.

Soda/O<sub>2</sub> cooks followed the same sequence of steps with the following modifications:

- a. The soda-impregnated straw was held in the digester for one hour at 90° C.
- b. The digester was pressurized to 75 psig with oxygen.
- c. Temperature was increased to 120° C for one hour of pulping.

Combinations of heating time, pulping time and alkali charges shown in Tables 1 and 2 for the two processes resulted in kappa numbers ranging from about 12 to about 45. The influence of pulping variables on pulping results is discussed later.

Unbleached soda/AQ and soda/O<sub>2</sub> pulps at kappa 16 and 12 respectively were converted to handsheets for testing. The same pulps were treated by the bleaching sequences shown in Figure 19 with conditions and results described later.

### **Soda/AQ Pulping -- Liquid Phase**

Presteamed straw in the digester was covered with soda/AQ liquid at 8/1 liquid/OD straw (L/W) heated to 170°C.

**Table 21. Metals in Internodes (ppm)**

	Madsen 1	Madsen 2	Madsen 3	Madsen 4	Madsen avg.	Eltan	Stephens	Lewjain	Cashup	Rod
Al	<20	<20	<20	<20	<20	20	<20	<20	<20	<20
B	<20	<20	<20	<20	<20	<20	<20	<20	<20	<20
Ba	83	36	38	36	48.25	28	30	50	62	58
Ca	3300	2030	1550	1130	2002.5	2510	2330	1960	1780	2530
Cr	<1	<1	<1	<1	<1	<1	<1	<1	<1	<1
Cu	5	4	3	3	3.75	3	3	4	3	3
Fe	28	54	44	42	42	59	41	21	87	37
K	34000	15000	19000	23000	22750	13000	22000	20000	20000	21000
Mg	2970	920	700	640	1307.5	730	620	500	680	560
Mn	19.8	14.9	18.4	10.4	15.875	12	15.6	15.4	25.1	14.5
Mo	2	<1	<1	<1		<1	1	<1	<1	<1
Na	260	160	60	60	135	430	230	280	390	150
P	1020	520	750	1030	830	420	480	330	400	440
Sn	6	<5	5	5		6	<5	6	5	5
Sr	15.9	10.8	7.6	5.8	10.025	9.1	13.9	10.4	11.8	11.8
Zn	24	14	12	15	16.25	10	11	7	13	7

**Table 22. Metals in Nodes (ppm)**

	Madsen 1	Madsen 2	Madsen 3	Madsen 4	Madsen avg.	Eltan	Stephens	Lewjain	Cashup	Rod
Al	<20	<20	<20	<20	<20	<20	<20	20	<20	<20
B	<20	<20	<20	<20	<20	<20	<20	<20	<20	<20
Ba	54	62	78	80	68.5	40	39	97	72	67
Ca	2400	3200	3050	2850	2875	2500	3240	3080	2200	3470
Cr	<1	<1	<1	<1	<1	<1	<1	<1	<1	<1
Cu	5	13	5	3	6.5	5	4	9	6	4
Fe	36	23	26	68	38.25	26	25	43	22	25
K	20000	23000	32000	39000	28500	34000	30000	65000	34000	40000
Mg	1700	2720	2770	2200	2347.5	1320	1230	1220	930	1150
Mn	20.1	17.3	18.4	9.9	16.425	9.3	15.6	27.2	23	12.4
Mo	1	1	2	1	1.25	1	2	2	1	1
Na	400	770	230	50	362.5	680	910	1570	880	440
P	780	800	940	910	857.5	350	580	1020	410	490
Sn	5	6	5	7	5.75	<5	<5	6	<5	<5
Sr	11.9	17.2	14.9	12.4	14.1	9.6	18.8	15.4	13.7	15.7
Zn	24	24	22	25	23.75	16	12	25	21	13

**Table 23. Metals in Leaves (ppm)**

	Madsen 1	Madsen 2	Madsen 3	Madsen 4	Madsen avg.	Eltan	Stephens	Lewjain	Cashup	Rod
Al	60	100	50	50	50	50	60	60	40	50
B	<20	<20	<20	<20	<20	<20	30	30	30	30
Ba	80	86	79	77	80.5	47	67	65	71	75
Ca	6750	7550	7230	6530	7015	7040	8230	6250	5950	6990
Cr	<1	<1	<1	<1	<1	<1	<1	<1	3	1
Cu	4	5	5	5	4.75	5	5	6	5	4
Fe	120	175	116	96	126.75	159	127	139	88	106
K	11000	6000	13000	18000	12000	9000	10000	11000	13000	11000
Mg	2420	2790	2510	2180	2475	2030	2640	2220	2360	2000
Mn	70.1	125	90.4	45.8	82.825	34.9	128	66.4	119	60
Mo	<1	1	1	1		<1	1	<1	<1	<1
Na	50	70	70	60	62.5	70	100	90	130	100
P	1140	920	1620	1530	1302.5	1440	1330	1710	1330	1060
Sn	<5	5	6	<5		7	<5	<5	<5	<5
Sr	25.4	30.3	26.4	22.8	26.225	22.1	37.8	23.7	28.7	23.5
Zn	17	21	15	16	17.25	19	20	24	17	18